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SOME THERMODYNAMIC CONSTANTS OF ALKALI METANIOBATES AND METATANTALATES

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ABSTRACT: A method for computing the radii of NbO^-_3 and TaO^-_3 ions using data on the solubility of alkali metaniobates and metatantalates is discussed, and the results are tabulated.

While doing systematic research on various tantalates and niobates we /25* found we would have to use the value of the radii of metaniobate and metatantalate ions in some of the computations. We were unable to find the magnitudes of these radii in the literature, however, A. Ye. Fersman [1] introduces a value of 1.40 Å for the magnitude of the radii of these ions (for both ions), something that clearly contradicts the realities of the situation. A. V. Lapitskiy and B. D. Nebylitsyn cite a magnitude of 1.76 Å [2], one that apparently is in better concordance with the true value. However, the method they use to estimate the magnitudes of the radii is very approximate.

In view of the foregoing, we decided to compute the radii of NbO^-_3 and TaO^-_3 ions by using data on the solubility of alkali metaniobates and metatantalates [3, 4].

We computed the values of change in the free energy (the Gibbs free energy) as a result of the formation of anhydrous alkali metaniobates and metatantalates from their ions, and their heats of solution. The data obtained were used to find the radii of the NbO_3^- and TaO_3^- ions, their heats of hydration, and the energy of the crystal lattices formed by the meta-salts. The data required for the computation were taken from previously published papers [3, 4].

The results of the computations are listed in the accompanying table. The radius of the niobate ion was found to be equal to 2.04 Å, and its heat of hydration to be equal to 95 kcal/mole. The corresponding magnitudes for

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* Numbers in the margin indicate pagination in the foreign text.

the tantalate ion were 1.83 Å and 110 kcal/mole.

The method used for the computation was as follows. Solubility at 20° and 30° was established by a straight line extrapolation in logS - 1/T coordinates. The activity product at 25° was computed in concordance with the theory of strong electrolytes [5]. The change in the Gibbs free energy was computed through the generally known formula

$$\Delta F_{298} = RT \log La.$$

The Van't Hoff isochor equation was used to compute the heat of solution. /26
This equation, $d \log k/dT = -(\varphi/RT^2)$, can be rewritten in the following form as applicable to salts

$$\frac{d \log La}{dT} = -\frac{\lambda}{RT_1T_2}, \text{ or}$$

$$\lambda = -\frac{RT_1 \cdot T_2 \cdot d \log La}{dT},$$

where

λ is the heat of solution;

La is the activity product;

T is the absolute temperature;

R is the gas constant.

It can be taken that λ, the differential heat of solution, is equal to the /27
integral heat of solution in the case of salts that are not readily soluble.

The niobate and tantalate ion radii were computed by the simultaneous solution of Kapustinskiy and Fajans equations [7]. The fourth power equation obtained was solved by the successive substitutions method. Fajans equation was used to find the heat of hydration [7].

TABLE

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Substance	Temperature, °C	Solubility, S, m/l	Activity product La	Change in free energy, ΔF°	Heat of solution λ	Energy of crystal lattice, U_c
				kcal/mole		
$LiNbO_3$	20	$2,566 \cdot 10^{-4}$	$6,344 \cdot 10^{-8}$	9,7	6,2	228,5
	25	$2,800 \cdot 10^{-4}$	$7,539 \cdot 10^{-8}$			
	30	$3,060 \cdot 10^{-4}$	$8,988 \cdot 10^{-8}$			
$NaNbO_3$	20	$4,803 \cdot 10^{-4}$	$2,192 \cdot 10^{-7}$	8,8	14,4	211,9
	25	$5,900 \cdot 10^{-4}$	$3,289 \cdot 10^{-7}$			
	30	$7,269 \cdot 10^{-4}$	$4,962 \cdot 10^{-7}$			
$KNbO_3$	20	$6,726 \cdot 10^{-4}$	$4,258 \cdot 10^{-7}$	8,4	18,8	187,8
	25	$8,700 \cdot 10^{-4}$	$7,065 \cdot 10^{-7}$			
	30	$1,157 \cdot 10^{-3}$	$1,237 \cdot 10^{-6}$			
$RbNbO_3$	20	$9,687 \cdot 10^{-5}$	$9,171 \cdot 10^{-9}$	10,8	9,3	178,7
	25	$1,100 \cdot 10^{-4}$	$1,181 \cdot 10^{-8}$			
	30	$1,261 \cdot 10^{-4}$	$1,549 \cdot 10^{-8}$			
$CsNbO_3$	20	$7,796 \cdot 10^{-5}$	$5,952 \cdot 10^{-9}$	11,1	7,8	170,1
	25	$8,700 \cdot 10^{-5}$	$7,408 \cdot 10^{-9}$			
	30	$9,738 \cdot 10^{-5}$	$9,268 \cdot 10^{-9}$			
$LiTaO_3$	20	$8,974 \cdot 10^{-5}$	$7,878 \cdot 10^{-9}$	10,9	10,5	249,1
	25	$1,050 \cdot 10^{-4}$	$1,077 \cdot 10^{-8}$			
	30	$1,211 \cdot 10^{-4}$	$1,429 \cdot 10^{-8}$			
$NaTaO_3$	20	$4,679 \cdot 10^{-5}$	$2,153 \cdot 10^{-9}$	11,6	10,7	229,6
	25	$5,460 \cdot 10^{-5}$	$2,929 \cdot 10^{-9}$			
	30	$6,342 \cdot 10^{-5}$	$3,949 \cdot 10^{-9}$			
$KTaO_3$	20	$3,959 \cdot 10^{-5}$	$1,541 \cdot 10^{-9}$	11,8	14,3	201,6
	25	$4,870 \cdot 10^{-5}$	$2,333 \cdot 10^{-9}$			
	30	$5,936 \cdot 10^{-5}$	$3,460 \cdot 10^{-9}$			
$RbTaO_3$	20	$3,219 \cdot 10^{-5}$	$1,022 \cdot 10^{-9}$	12,0	12,3	191,0
	25	$3,840 \cdot 10^{-5}$	$1,454 \cdot 10^{-9}$			
	30	$4,567 \cdot 10^{-5}$	$2,054 \cdot 10^{-9}$			
$CsTaO_3$	20	$2,728 \cdot 10^{-5}$	$7,353 \cdot 10^{-10}$	12,3	8,4	181,4
	25	$3,080 \cdot 10^{-5}$	$9,365 \cdot 10^{-10}$			
	30	$3,467 \cdot 10^{-5}$	$1,185 \cdot 10^{-9}$			

Commas represent decimal points.

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